

NEW INSIGHTS INTO THE ORIGIN OF MAGNETITE CRYSTALS IN ALH84001 CARBONATE DISKS

K. L. Thomas-Keprta¹, S. J. Clemett¹, S.J. Wentworth¹, D.S. McKay², E.K. Gibson, Jr.², ¹ESCG at NASA/JSC, Mail Code JE23, Houston, TX 77058 (kathie.thomas-keprta-1@nasa.gov), ²ARES, NASA/JSC, Mail Code KR, Houston, TX 77058.

Introduction: Martian meteorite ALH84001 preserves evidence of interaction with aqueous fluids while on Mars in the form of microscopic carbonate disks believed to have formed ~3.9 Ga ago at beginning of the Noachian epoch. Intimately associated within and throughout these carbonate disks are nanocrystal magnetites (Fe_3O_4) with unusual chemical and physical properties, whose origins have become the source of considerable debate. One group of hypotheses argues that these magnetites are the product of partial thermal decomposition of the host carbonate. Alternatively, the origins of magnetite and carbonate may be unrelated; that is, from the perspective of the carbonate the magnetite is allochthonous. We have sought to resolve between these hypotheses through the detailed characterization of the compositional and structural relationships between the carbonate disks, their associated magnetites and the orthopyroxene matrix in which they are embedded [1]. Comparison of these results with experimental thermal decomposition studies of sideritic carbonates conducted under a range of heating scenarios suggests that the magnetite nanocrystals in the ALH84001 carbonate disks are not the products of thermal decomposition.

Methods: *ALH84001*. In total, seven focused ion beam (FIB) transverse sections were extracted from two carbonate disks – three spanning the disk inner cores and four the thin rims which surround the cores. Extracted FIB sections were either *Pt*-welded *in situ* onto a *Cu* TEM crescent lift-out grid or placed *ex situ* onto a continuous *C* film *Cu* TEM grid. Sections were analyzed by high-resolution transmission electron microscopy (TEM) equipped with light element energy dispersive X-ray spectroscopy (EDX).

Roxbury Siderite. To investigate the chemical compositions of magnetite formed from the decomposition of *Fe*-rich carbonates, a sample of Roxbury siderite, having a bulk composition of $(Fe_{0.84}Mg_{0.10}Mn_{0.04}Ca_{0.02})CO_3$ [2], was decomposed using two different heating regimes – ‘slow’, (~10⁻² K/sec; identical to that used by [3]), and ‘fast’ (~10⁸-10⁹ K/sec) using a pulsed CO_2 laser to simulate the rapid heterogeneous heating characteristic of impact shock. An unheated sample served as a control. Unheated, ‘fast’ and ‘slow’ heated samples were embedded in epoxy and prepared for analysis by TEM using diamond knife ultramicrotomy.

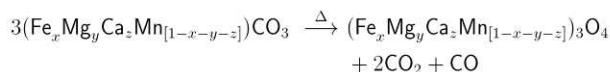
Results: *ALH84001*. Carbonate disks can be envisioned as being composed of three concentric annular zones; starting from the center there is an inner central and outer core surrounded by a thin rim

composed of optically alternating black-white-black layers. ALH84001 magnetites are embedded within all compositions of carbonate ranging from the most *Fe*-rich $(Fe_{0.60}Mg_{0.16}Mn_{0.04}Ca_{0.05})CO_3$ at the disk core to the most *Fe*-free magnesite (white layer in the rim zone; Fig. 1) with the highest population density occurring within the black layers of the rim zone. The majority of these magnetites are stoichiometrically pure Fe_3O_4 although there were several notable exceptions where a small fraction of magnetites contained minor to trace amounts of *Cr*, which was undetectable in the surrounding host carbonate (Fig.2). *Roxbury Siderite Control Sample*. Roxbury siderite is compositionally analogous to the *Fe*-rich component of ALH84001 carbonate disks, with a composition of $(Fe_{0.75}Mg_{0.24}Mn_{0.003}Ca_{0.004})CO_3$ as calculated by [4]. However, TEM characterization at the sub-micron scale of Roxbury siderite shows significant variations in *Fe:Mg* ratio relative to the bulk composition and appeared to be correlated with grain size. The fine grain (<100 nm) component is *Mg*-poor (*Fe:Mg* > 20:1) while, by comparison, the coarse grained component is *Mg*-rich (*Fe:Mg* < 8:1). In both size ranges *Mn* and *Ca* appeared relatively uniform in comparison.

Roxbury Siderite ‘Fast’ and ‘Slow’ Heated Samples. Under both ‘fast’ and ‘slow’ heating regimes, decomposition of Roxbury siderite resulted in the formation of impure ferrites with the *Mg* varying from one crystal to another while the *Mn* content remained invariant (Fig. 3). Since the *Mg* and *Mn* variation mirrors that of the unheated carbonate in magnitude and range, this variation is simply a reflection of the initial content of the carbonate (notably, in neither the ‘fast’ or ‘slow’ products did we find any evidence for discrete *MgO* or *CaO* phases).

These results, in conjunction with prior carbonate decomposition studies of the *Fe*-, *Mg*- and *Ca*-ternary carbonates (e.g., 5 – 6; references in [1]), show that the decomposition of impure, cation substituted siderites invariably yields impure *Fe*-oxides.

Discussion & Implications: Based on previous decomposition studies of mixed cation siderites and our decomposition studies of Roxbury siderite, the following summarizes the thermal decomposition reaction of mixed cation siderite and the composition of the resulting product phase:



Although thermal decomposition hypotheses for the observation of chemically pure magnetites in ALH84001 carbonate disks appears, on the surface, to provide a simple inorganic explanation of the observations, it is not applicable to the formation of the vast majority of ALH84001 magnetites. For example, it is difficult to suggest a process by which the magnesite, which is essentially *Fe*-free, decomposed to form magnetite. Furthermore, it would be difficult to explain the presence of chemically impure magnetites with minor to trace amounts of *Cr* since this element cannot substitute into the trigonal ($R\bar{3}c$) structure of carbonate.

Thermal decomposition of Roxbury siderite under *both* ‘fast’ and ‘slow’ heating resulted in the formation of impure (*Mg,Ca,Mn*)-ferrites. These findings agree with prior decomposition studies performed under a wide variety of conditions and are in stark contrast to the chemically pure magnetites characteristic of ALH84001 carbonate disks.

The presence of chemically pure ALH84001 magnetite is inconsistent with formation by thermal decomposition of the host carbonate. We suggest that the majority of ALH84001 magnetites has an allochthonous origin and was added to the carbonate system from an outside source. This origin does not exclude the possibility that a fraction is consistent with formation by biogenic processes, as proposed in previous studies.

References: [1] Thomas-Keprta *et al.* (2009) *GCA* **73**,6631-6677. [2] Lane, M. & Christensen, P. (1997) *JGR*, 102, 25581-25592. [3] Golden, D.C. *et al.* (2006) *LPSC XXXVII*, #1199. [4] Treiman, A.H. (2003) *Astrobiology*, 3, 369-392. [5] Jiménez López, C. *et al.* (2008) *AGU*, #P51A-1405. [6] Gotor, F.J. *et al.* (2000) *Phys. & Chem. of Min.*, 27, 495-503.

Fig.1. *Upper:* TEM view of ALH84001 magnetites (arrows) embedded within the magnesite layer. *Lower:* EDX spectra for one of the magnetites (red circle), the surrounding magnesite matrix (blue circle), and the difference spectrum (green). They show the host matrix is essentially *Fe*-free while the magnetite is *Mg*-free. The presence of these magnetites embedded in the magnesite band indicates they could not have formed by thermal decomposition of the magnesite matrix.

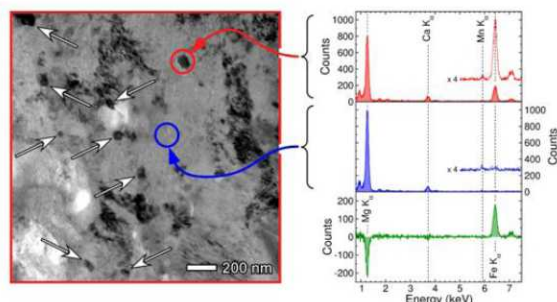


Fig.2. *Top views:* FIB section extracted from the core-rim interface of an ALH84001 carbonate disk (left) and high magnification of magnetite crystals within that section (right). *Bottom views:* Element maps for *Fe* (left) and *Cr* (right) of the largest magnetite in the field of view (top right). This magnetite has a composition of *Fe* ~70.1 wt.%, *Cr* ~ 2.3 wt.%, and *O* ~27.6 wt.%, corresponding to a stoichiometry of $(Fe_{2.9}Cr_{0.1})O_4$ (i.e., ~ 3.3% Cr_2O_3).

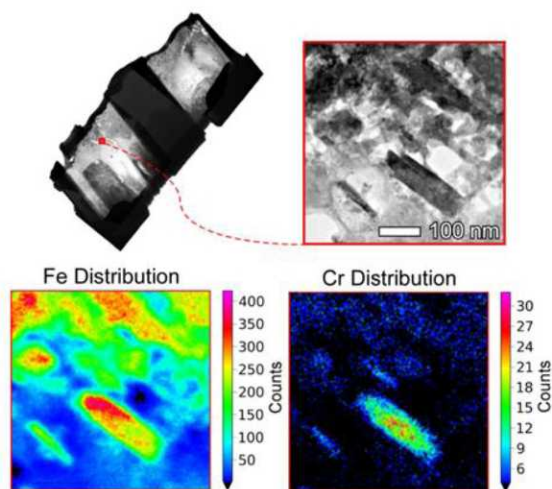


Fig. 3. EDX spectra and TEM views of magnetites formed from the ‘slow’ (green box) and ‘fast’ (blue box) heating of Roxbury siderite. Although spatially associated, variations in *Mg* content are apparent while *Mn* content is relatively uniform. All magnetites formed from the thermal decomposition of Roxbury siderite contained chemical impurities reflecting the composition of the precursor Roxbury siderite.

